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Vapor−Liquid Equilibrium, Densities, and Interfacial Tensions of the System Ethanol + Tetrahydro-2*H*-pyran

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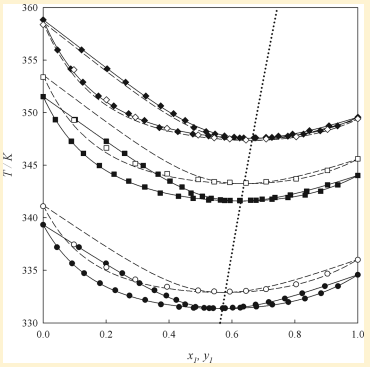
Supporting Information

ABSTRACT: Isobaric vapor−liquid equilibrium (VLE) data have been measured for the binary system ethanol + tetrahydro-2*H*-pyran at (50, 75, and 94) kPa and over the temperature range (331 to 358) K using a vapor−liquid equilibrium still with circulation of both phases. Mixing volumes were also determined at 298.15 K and atmospheric pressure with a vibrating tube densimeter, while a maximum differential bubble pressure tensiometer was used to measure atmospheric interfacial tensions at 303.15 K. According to experimental results, the mixture exhibits positive deviation from ideal behavior, and minimum boiling point azeotropy is present at mid-range concentrations ($0.55 < x_1^{Az} < 0.67$). VLE measurements show also that the azeotropic mole fraction impoverishes in ethanol as pressure (or temperature) increases. The mixing volumes of the mixture evolve from positive to negative deviations as the concentration of ethanol increases. Finally, it is experimentally observed that the interfacial tensions exhibit positive deviations from the linear behavior. The VLE data of the binary mixture satisfy Fredenlund's consistency test and were well-correlated by the Wohl, nonrandom two-liquid (NRTL), Wilson, and universal quasichemical (UNIQUAC) equations for all of the measured isobars. The mixing volumes and interfacial tensions, in turn, were satisfactorily correlated using the Redlich−Kister equation.



INTRODUCTION

Ethers (branched and cyclic) are considered some of the most important chemicals in the industry. Particularly, branched ethers (such as 2-methoxy-2-methylpropane or MTBE, 2-ethoxy-2-methyl-propane or ETBE, 2,2′-oxybis[propane] or DIPE, and 2-methoxy-2-methylbutane or TAME) have extensively been used as oxygenates in gasoline production. Cyclic ethers, in turn (e.g., tetrahydrofuran or THF, 1,4-dioxane, and tetrahydro-2*H*-pyran or THP), are frequently used as solvents in chemical and electrochemical processes, as well as basic reagents (i.e., monomer) for ring-opening polymerization, and for the production of other chemical intermediaries. Recently, industrial interest in using THP as a potentially attractive cyclic ether has increased due to new and economic production routes.[1−4]

Thermophysical properties of THP-based mixtures are useful for exploring their potential in the formulation of new alternatives for commercial fuels. In fact, detailed vapor−liquid equilibrium (VLE) data are needed for rationalizing the production of THP[1] at industrial scale, and additionally, they may provide useful information for characterizing the distillation curve (fuel concentration during vaporization) and the Reid vapor pressures (volatility indicator) for possible gasoline blending applications. Density data, in turn, are required for designing engine injection systems and for adequate vessels for fuel storage and transportation. Interfacial tension (IFT) data are needed to characterize the formation and ignition kinetics of fuel drops. Finally, VLE, density, and IFT data are important for assessing the environmental impact of organic mixtures in air, ground, and aquifers. In fact, IFTs define the wettability patterns of fluid systems in aquifers and soils, thus providing a route to rationalize environmental remediation methods.

In spite of their potential relevance, and compared to the case of more traditional cyclic ethers,[5−7] few experimental works have been devoted to characterize the thermophysical properties of THP mixtures. In general, we have observed that available data for THP + *n*-alkane and + alcohol mixtures are scarce and incomplete. Only Uno et al.[8] have reported boiling temperatures and liquid phase mole fractions from (40 to 98) kPa for ethanol + THP. According to that data, the mixture exhibits positive deviation from ideal behavior, and additionally, an azeotrope is present. To the best of our knowledge, neither mixing volumes (or excess volumes, V^E) nor IFT data have been previously reported for THP-based mixtures.

This contribution is undertaken to experimentally determine new and accurate data for the phase equilibrium, mixing densities, and atmospheric interfacial tensions of ethanol + THP, thus contributing to the thermophysical characterization of THP + polar solvents.

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Table 1. Gas Chromatography (GC) Purities (Mass Fraction), Refractive Index (n_D) at Na D line, Densities (ρ), Normal Boiling Points (T_b), and Interfacial Tensions (σ) of Pure Components

	n_D		ρ/g·cm^{-3}		T_b/K		σ/mN·m^{-1}	
	T/K = 298.15		T/K = 298.15		p/kPa = 101.33		T/K = 303.15	
component (purity/mass fraction)	exp.	lit.	exp.	lit.	exp.	lit.	exp.	lit.
ethanol (0.999)	1.36068	1.35940[a]	0.78509	0.78589[a]	351.45	351.44[a]	21.7	21.68[a]
THP (0.998)	1.42000	1.41950[b]	0.87903	0.87880[c]	361.36	361.31[d]	27.1	26.66[e]

[a]Daubert and Danner.[9] [b]Riddick et al.[10] [c]Giner et al.[11] [d]Gill et al.[12] [e]Interpolated data from Villares et al.[13]

EXPERIMENTAL SECTION

Chemicals. Ethanol (Merck) and tetrahydro-2*H*-pyran (Aldrich) were used as received, without considering additional purification. Table 1 reports the purity of the components (as determined by gas chromatography, GC), together with the normal boiling points of the pure fluids (T_b), the mass densities (ρ), the refractive indexes (n_D) at 298.15 K, and the interfacial tensions (σ) of pure fluids at 303.15 K. The reported values are also compared with those reported in the literature.[9−13]

Apparatus and Procedure. VLE data were determined by using an all-glass VLE cell model 601 (Fischer Labor and Verfahrenstechnik). The temperature accuracy was ± 0.02 K, whereas the pressure was measured with an estimated accuracy of ± 0.03 kPa. Densities were measured using a Anton Paar DMA 5000 vibrating U-tube densimeter. The accuracy of density measurements was $5\cdot10^{-6}$ g·cm^{-3}, and the temperature of the apparatus was maintained constant to within ± 0.01 K. The refractive indexes were measured using a multiscale automatic refractometer RFM 81 (Bellingham and Stanley). The uncertainties in measurements are ± 10^{-5}, and the temperature was kept constant to within ± 0.01 K. Interfacial tensions were measured using a Sensadyne maximum differential bubble pressure tensiometer model PC500-LV. The temperature of the sample in the vessel was kept constant to within ± 0.01 K using a Julabo thermostatic bath, conditions in which interfacial tension measurements were accurate within ± 0.01 mN·m^{-1}. Specific details concerning the experimental procedures have been described in depth in recent works;[14−17] so briefly, we constrain our description to key operating parameters. Temperature conditions in gas chromatography were (373.15, 393.15, and 493.15) K for column, injector, and detector, respectively, conditions in which concentration measurement accuracies were better than ± 0.001 in mole fraction. Additional details concerning to the VLE technique have been extensively described by Raal and Mühlbauer,[18] whereas maximum differential bubble pressure technique have been described by Adamson and Gast[19] and Rusanov and Prokhorov.[20]

RESULTS AND DISCUSSION

Vapor−Liquid Equilibrium. The boiling temperature T, the liquid x_i, and vapor-phase y_i mole fractions of component i at P = (50, 75, and 94) kPa are reported in Tables 2 to 4 and illustrated in Figure 1 (solid symbols). Tables 2 to 4 also include the activity coefficients (γ_i), which are displayed in Figures S1 to S3 in the Supporting Information and were calculated from the following equation:[21]

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \quad (1)$$

Table 2. Experimental VLE Data for Ethanol (1) + THP (2) at P = 50.00 kPa[a]

T					$-B_{ij}$/cm^3·mol^{-1}		
K	x_1	y_1	γ_1	γ_2	11	22	12
339.33	0.000	0.000		1.000		1258	
337.19	0.044	0.114	2.346	0.998	1170	1279	710
335.65	0.092	0.200	2.095	1.001	1196	1295	718
334.72	0.130	0.251	1.939	1.011	1212	1305	723
333.77	0.181	0.306	1.770	1.029	1229	1315	728
333.11	0.229	0.354	1.658	1.044	1241	1322	732
332.60	0.275	0.391	1.565	1.064	1250	1328	734
332.19	0.324	0.423	1.458	1.100	1257	1332	737
331.77	0.375	0.452	1.371	1.148	1265	1337	739
331.52	0.432	0.484	1.288	1.200	1270	1340	740
331.43	0.479	0.512	1.233	1.242	1271	1341	741
331.40	0.528	0.540	1.181	1.293	1272	1341	741
331.40	0.578	0.571	1.138	1.354	1272	1341	741
331.45	0.627	0.602	1.106	1.414	1271	1341	741
331.55	0.678	0.636	1.075	1.493	1269	1340	740
331.74	0.728	0.675	1.052	1.574	1266	1337	739
331.99	0.779	0.717	1.032	1.675	1261	1335	738
332.31	0.832	0.768	1.020	1.786	1255	1331	736
332.82	0.883	0.824	1.007	1.922	1246	1326	733
333.49	0.937	0.896	1.002	2.069	1234	1318	730
334.57	1.000	1.000	1.000		1214		

[a]T is the equilibrium temperature; x_i and y_i are mole fractions in liquid and vapor phases of component i, respectively. γ_i are the activity coefficients of component i, and B_{ij} are the molar virial coefficients.

where P is the total pressure and P_i^0 is the pure component vapor pressure. R is the universal gas constant. V_i^L is the liquid molar volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and the mixing rule of second virial coefficients (δ_{ij}) is given by $\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii}$.

Equation 1 is valid from low to moderate pressures, where the virial equation of state truncated after the second term is adequate for describing the vapor phase of the pure components and their mixtures and, additionally, the liquid molar volumes of pure components are incompressible over the pressure range under consideration. Liquid molar volumes were estimated from the correlation proposed by Rackett.[22] Critical properties were taken from Riddick et al.[10] The molar virial coefficients B_{ii}, B_{jj}, and B_{ij} were estimated by the method of Hayden and O'Connell[23] using the molecular and solvation parameters η suggested by Prausnitz et al.[24] for ethanol. For the case of THP, molecular parameters and physical properties were also taken from ref 10. THP's solvation parameter η was estimated by smoothing experimental data of second virial coefficients reported in ref 25, thus yielding the value η = 0.05. Pure component and cross virial coefficients are reported in Tables 2 to 4.

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Table 3. Experimental VLE Data for Ethanol (1) + THP (2) at P = 75.00 kPa[a]

T					$-B_{ij}$/cm^3·mol^{-1}		
K	x_1	y_1	γ_1	γ_2	11	22	12
351.53	0.000	0.000		1.000		1145	
349.33	0.038	0.102	2.190	1.000	993	1164	651
347.28	0.090	0.200	1.992	1.004	1020	1182	660
346.13	0.128	0.259	1.882	1.009	1035	1193	665
344.97	0.178	0.318	1.735	1.023	1051	1203	671
344.14	0.225	0.365	1.629	1.039	1063	1211	675
343.49	0.272	0.403	1.526	1.063	1072	1217	678
342.92	0.323	0.441	1.439	1.091	1081	1223	681
342.34	0.372	0.470	1.360	1.138	1089	1228	684
342.04	0.430	0.506	1.283	1.181	1094	1231	685
341.84	0.477	0.534	1.231	1.222	1097	1233	686
341.70	0.526	0.563	1.182	1.272	1099	1234	687
341.65	0.577	0.594	1.139	1.327	1100	1235	687
341.64	0.626	0.625	1.103	1.391	1100	1235	687
341.67	0.676	0.659	1.075	1.459	1099	1235	687
341.77	0.727	0.696	1.051	1.541	1098	1234	687
341.92	0.778	0.737	1.033	1.631	1095	1232	686
342.16	0.833	0.786	1.019	1.754	1092	1230	685
342.52	0.882	0.838	1.010	1.866	1087	1226	683
343.12	0.936	0.904	1.001	2.011	1078	1221	680
344.02	1.000	1.000	1.000		1065		

[a] T is the equilibrium temperature; x_i and y_i are mole fractions in liquid and vapor phases of component i, respectively. γ_i are the activity coefficients of component i, and B_{ij} are the molar virial coefficients.

Table 4. Experimental VLE Data for Ethanol (1) + THP (2) at P = 94.00 kPa[a]

T					$-B_{ij}$/cm^3·mol^{-1}		
K	x_1	y_1	γ_1	γ_2	11	22	12
358.85	0.000	0.000		1.000		1085	
355.97	0.046	0.122	2.123	1.001	913	1108	621
354.17	0.088	0.203	1.971	1.004	934	1123	629
352.91	0.126	0.262	1.851	1.009	949	1133	635
351.58	0.176	0.326	1.737	1.018	965	1145	641
350.65	0.225	0.374	1.612	1.036	976	1153	645
349.91	0.272	0.414	1.519	1.056	985	1159	648
349.26	0.322	0.451	1.429	1.086	994	1165	651
348.58	0.369	0.479	1.357	1.133	1002	1171	654
348.20	0.428	0.518	1.284	1.171	1007	1174	656
347.97	0.476	0.546	1.228	1.213	1011	1176	657
347.79	0.526	0.576	1.180	1.260	1013	1178	658
347.66	0.576	0.607	1.139	1.314	1015	1179	658
347.60	0.625	0.638	1.105	1.374	1015	1179	659
347.60	0.676	0.670	1.074	1.447	1015	1179	659
347.65	0.727	0.708	1.053	1.519	1015	1179	658
347.77	0.778	0.748	1.032	1.613	1013	1178	658
347.96	0.828	0.793	1.020	1.700	1011	1176	657
348.28	0.881	0.846	1.010	1.811	1006	1173	655
348.75	0.936	0.908	1.002	1.984	1000	1169	653
349.56	1.000	1.000	1.000		990		

[a] T is the equilibrium temperature; x_i and y_i are mole fractions in liquid and vapor phases of component i, respectively. γ_i are the activity coefficients of component i, and B_{ij} are the molar virial coefficients.

The vapor pressures of pure components were experimentally determined as a function of temperature using the same equipment as that for obtaining the VLE data. Table 5 reports

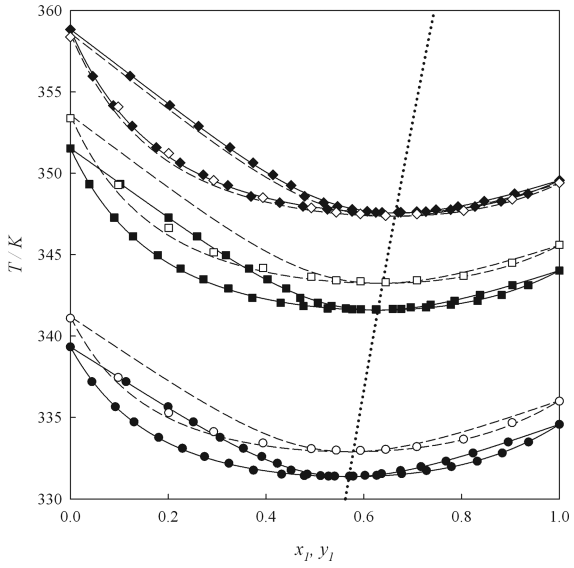

Figure 1. Isobaric phase diagram for the system ethanol (1) + THP (2). Experimental data at ●, 50.0 kPa; ■, 75.0 kPa; ♦, 94.0 kPa. Experimental data reported by Uno et al.[8] at ○, 53.33 kPa; □, 79.99 kPa; ◊, 93.32 kPa; —, predicted from the two-parameter Legendre polynomial used in consistency analysis; - - -, predicted from the Wohl model with the parameters indicated in Table 8; ···, azeotropic line.

Table 5. Experimental Vapor Pressures (P) as a Function of Temperature (T) for THP

T/K	P/kPa
312.59	18.01
319.62	24.01
325.36	30.01
331.70	38.0
336.40	45.0
339.98	51.0
344.26	59.0
347.64	66.0
350.74	73.0
353.61	80.0
356.29	87.0
358.81	94.0
361.55	102.1

Table 6. Estimated Azeotropic Coordinates for the System Ethanol (1) + THP (2)[a]

P/kPa	x_1^{Az}	T^{Az}/K
50.00	0.570	331.37
75.00	0.629	341.59
94.00	0.665	347.56

[a] P is the pressure of the system; x_1^{Az} is the azeotropic mole fraction, and T^{Az} is the azeotropic temperature.

the experimental values obtained for the vapor pressures of THP, whose dependence on temperature can be accurately correlated by using the Antoine equation:

$$\log(P_i^0/\text{kPa}) = 5.60624 - 1010.3546/[(T/\text{K}) - 80.7458] \quad (2)$$

Equation 2 correlates P_i^0 data of THP from (321.59 to 360) K with an average of the absolute percentage deviation (AAPD)

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Table 7. Consistency Test Statistics for the Binary System Ethanol (1) + THP (2)

P/kPa	L_1[a]	L_2[a]	100 Δy[b]	δP[c]/kPa
50.00	0.8442	−0.0425	0.3	0.1
75.00	0.8044	−0.0201	0.2	0.1
94.00	0.7858	−0.0105	0.3	0.2

[a]Parameters for the Legendre polynomial[28] used for consistency. [b]Average absolute deviation in vapor-phase mole fractions $\Delta y = (1/N)\sum_{i=1}^{N}|y_i^{exp} - y_i^{cal}|$ (N: number of data points). [c]Average absolute deviation in vapor pressure $\delta P = (1/N)\sum_{i=1}^{N}|P_i^{exp} - P_i^{cal}|$.

of 0.30 %. The reliability of eq 2 for predicting vapor pressures of THP has been successfully tested against the data reported by Miyano et al.[26] with an AAPD of 0.5 %. For the case of ethanol, experimental vapor pressures have been previously reported,[14] and their temperature dependence was obtained from:[14]

$$\log(P_i^0/\text{kPa}) = 7.16178 - 1549.6973/[(T/\text{K}) - 50.890] \quad (3)$$

The experimental data reported in Tables 2 to 4 allow the conclusion that the binary mixture exhibits positive deviation from ideal behavior and azeotropic behavior is present for each isobar. From Figure 1 we can conclude a good coherency between the present VLE data and those reported by Uno et al.[8] Azeotropic concentrations of the measured binary were estimated by fitting the empirical function

$$f(x) = 100\left(\frac{y - x}{x}\right) \quad (4)$$

where x and y have been taken from the experimental data. Azeotropic concentrations, as determined by solving $f(x) = 0$, are indicated in Table 6, where it is concluded that the mole fraction of the azeotrope impoverishes in ethanol as pressure (or temperature) increases, as it is shown in Figure 1. As it was observed with the general trend of the VLE data, the reported azeotropic coordinates are in good agreement with results presented by Uno et al.[8]

The VLE data reported in Tables 2 to 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al.[27] as modified by Fredenslund et al.[28] For each isobaric condition, the consistency criterion ($\Delta y < 0.01$) was met by fitting the equilibrium vapor pressure according to Barker's[29] reduction method. Statistical analysis[30] reveals that a two-parameter Legendre polynomial is adequate for fitting the equilibrium vapor pressure in each case. Pertinent consistency statistics and Legendre polynomial parameters are presented in Table 7. The activity coefficients presented in Tables 2 and 4 are estimated to be accurate to within 0.9 %.

Table 9. Densities (ρ) and Excess Volumes (V^E) as a Function of the Liquid Mole Fraction (x_1) for the Binary System Ethanol (1) + THP (2) at 298.15 K and 101.3 kPa

	ρ	$10^3 \cdot V^E$
x_1	g·cm^3	cm^3·mol^{-1}
0.000	0.87903	0
0.030	0.87714	19
0.115	0.87186	41
0.193	0.86685	45
0.299	0.85954	40
0.426	0.84989	24
0.496	0.84401	14
0.599	0.83465	0
0.716	0.82274	−11
0.799	0.81313	−15
0.910	0.79860	−12
0.959	0.79141	−6
1.000	0.78511	0

The VLE data reported in Tables 2 to 4 were correlated with the Wohl, nonrandom two-liquid (NRTL), Wilson, and universal quasichemical (UNIQUAC) equations,[31] whose adjustable parameters were obtained by minimizing the following objective function (OF):

$$\text{OF} = \sum_{i=1}^{N}(|P_i^{exp} - P_i^{cal}|/P_i^{exp} + |y_i^{exp} - y_i^{cal}|)^2 \quad (5)$$

In eq 5, the superscript exp stands for experimental data, while cal means calculated quantity. N is the number of data points. The parameters of the different activity coefficient models are reported in Table 8, together with the relative

Table 8. Parameters and Prediction Statistics for Different Gibbs Excess (G^E) Models in Ethanol (1) + THP (2)[a]

					bubble-point pressures		dew-point pressures	
model	P/kPa	A_{12}	A_{21}	α_{12}	ΔP (%)[b]	100 Δy_i[c]	ΔP (%)[b]	100 Δx_i[c]
Wohl	50.0	0.911	0.781	1.448[d]	0.3	0.2	0.3	0.2
	75.0	0.837	0.752	1.516[d]	0.2	0.1	0.3	0.1
	94.0	0.804	0.735	1.568[d]	0.2	0.1	0.2	0.1
NRTL	50.0	732.06	1915.30	0.400[e]	0.3	0.2	0.3	0.2
	75.0	820.80	1753.95	0.400[e]	0.3	0.1	0.3	0.2
	94.0	837.97	1705.52	0.400[e]	0.2	0.1	0.3	0.1
Wilson[f]	50.0	3231.40	−506.80		0.3	0.2	0.3	0.3
	75.0	3097.38	−458.91		0.3	0.2	0.3	0.2
	94.0	3056.91	−455.12		0.2	0.2	0.3	0.2
UNIQUAC[g]	50.0	−764.81	2224.63		0.3	0.2	0.3	0.2
	75.0	−739.41	2143.85		0.3	0.1	0.3	0.2
	94.0	−743.41	2130.02		0.2	0.1	0.3	0.1

[a]A_{12} and A_{21} are the G^E model parameters in J·mol^{-1}. [b]$\Delta P = (100/N)\sum_i^N|P_i^{exp} - P_i^{cal}|/P_i^{exp}$. [c]$\Delta\delta = 1/N\sum_i^N|\delta_i^{exp} - \delta_i^{cal}|$ with $\delta = y$ or x. [d]q parameter for the Wohl model. [e]α_{12} parameter for the NRTL model. [f]Liquid molar volumes have been estimated from the Rackett equation.[22] [g]The molecular parameters r and q are those reported in DECHEMA:[5] $r_1 = 2.1055$, $r_2 = 3.6159$, $q_1 = 1.9720$, $q_2 = 2.9400$.

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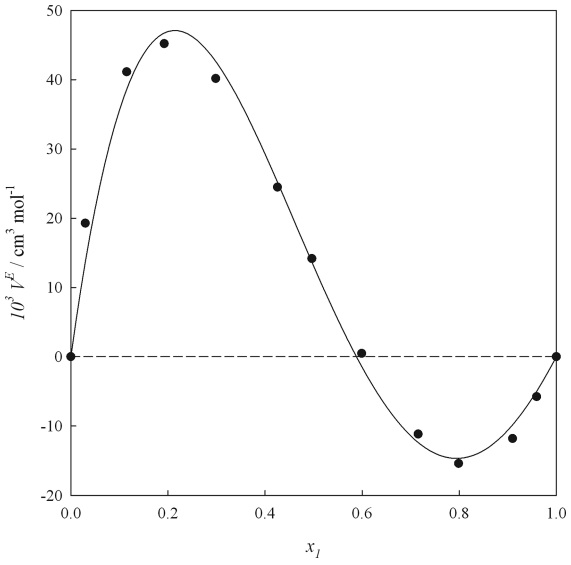

Figure 2. Excess volumes (V^E) as a function of the liquid phase (x_1) for the system ethanol (1) + THP (2) at 298.15 K and 101.3 kPa. ●, Experimental data; —, smoothed by the three-parameter Redlich–Kister expansion (see eq 7).

Table 10. Interfacial Tensions (σ) as a Function of the Liquid Mole Fraction (x_1) for the Binary System Ethanol (1) + THP (2) at 303.15 K and 101.3 kPa

	σ
x_1	mN·m^{-1}
0.000	27.10
0.068	26.91
0.122	26.76
0.223	26.50
0.323	25.98
0.420	25.34
0.520	24.90
0.604	24.35
0.622	24.24
0.657	24.07
0.707	23.81
0.722	23.64
0.821	23.01
0.918	22.42
0.963	22.00
1.000	21.70

deviation for the case of bubble- and dew-point pressures. From the results presented in Table 8, it is possible to conclude that all of the fitted models gave a reasonable correlation of the binary system and that the best fit is obtained with the Wohl model. The capability of simultaneously predicting the bubble- and dew-point pressures and the vapor- and liquid-phase mole fractions, respectively, has been used as the ranking factor. To establish the coherency of the present binary data and to test the predictive capability of the parameters reported in Table 8, we have used the best-ranked model (Wohl's model) to predict available VLE data. As it is illustrated in Figure 1, the quoted Wohl's parameters predict with fair accuracy the isobaric (T, x) data reported by Uno et al.[8] (open symbols).

According to the previous results, we can conclude that the Gibbs excess (G^E) parameters reported in this work can be used to accurately and consistently predict the VLE of the binary system.

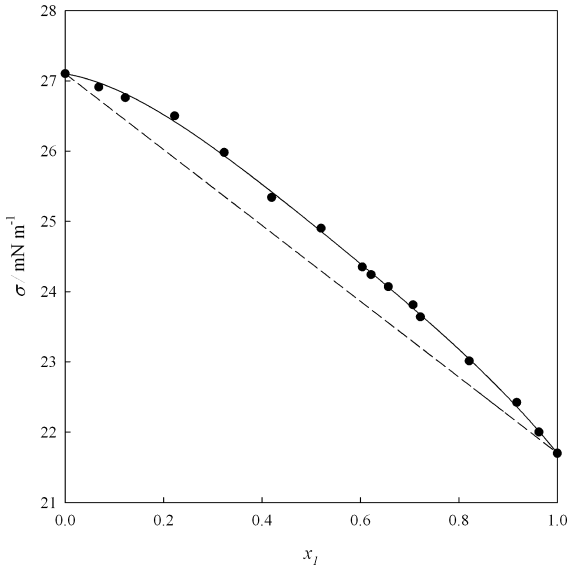

Figure 3. Interfacial tension (σ) as a function of the liquid mole fraction (x_1) for the system ethanol (1) + THP (2) at 303.15 K and 101.3 kPa. ●, experimental data; - - -, linear behavior ($x_1\sigma_1 + x_2\sigma_2$); —, smoothed by the three-parameter Redlich–Kister expansion (see eq 8).

Excess Volume Data. Table 9 reports the experimental density data for the mixture and its pure constituents at T = 298.15 K and P = 101.3 kPa. These density data allow calculating the excess volumes (V^E) of the mixture according to

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - x_1\frac{M_1}{\rho_1} - x_2\frac{M_2}{\rho_2} \quad (6)$$

In eq 6, ρ is the mass density of the mixture, while ρ_i corresponds to the mass density of the pure components (that have been reported in Table 1) and M_i is the molecular weight of the constituents that were taken from refs 9 and 10. The calculated V^E are estimated accurate to within ± 10^{-3} cm^3·mol^{-1}.

According to the results presented in Table 9 and Figure 2, it is possible to conclude that the excess volumes of the system are almost negligible, showing a sharp change from a slight positive to negative deviation as the concentration of ethanol increases. To assess the coherency of their trend, V^E data have been correlated by using a three-parameter Redlich–Kister expansion:[32]

$$(V^E/\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2[0.052384 + 0.320883(x_2 - x_1) + 0.13493(x_2 - x_1)^2] \quad (7)$$

The model reported in eq 7 is characterized by a maximum deviation of $3.0\cdot10^{-5}$ cm^3·mol^{-1}, an average deviation of $4.0\cdot10^{-6}$ cm^3·mol^{-1}, and a standard deviation of $8.0\cdot10^{-6}$ cm^3·mol^{-1}.

Interfacial Tension Data. The interfacial tension measurements for the mixture and its pure constituents at T = 303.15 K and P = 101.3 kPa are reported in Table 10 and in Figure 3. Experimental data were correlated using a three-parameter Redlich–Kister expansion:[33]

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$$(\sigma/\mathrm{mN{\cdot}m^{-1}}) = x_1x_2[2.2793 + 0.5220(x_2 - x_1) + 1.4316(x_2 - x_1)^2] + (x_1\sigma_1 + x_2\sigma_2) \quad (8)$$

Equation 8 yields a maximum deviation of $6.6{\cdot}10^{-3}$ mN·m^{-1} and an average deviation and a standard deviation of $2.1{\cdot}10^{-3}$ mN·m^{-1}. From Figure 3, it is possible to conclude that the interfacial tensions of the mixture ethanol + THP exhibit positive deviations from the lineal behavior ($x_1\sigma_1 + x_2\sigma_2$).

CONCLUSIONS

Isobaric VLE data at (50, 75, and 94) kPa, atmospheric mixing volumes at 298.15 K, and interfacial tensions at 303.15 K have been measured for ethanol + THP. Experimental VLE data reveal that the binary mixture exhibits positive deviations from ideal behavior and azeotropic behavior is present. The mole fraction of the azeotrope decreases in ethanol as the pressure (or temperature) increases, in good agreement with previous measurements.[8] Excess volumes exhibit a change from a slight positive to a negative deviation from the ideal behavior as the concentration of ethanol increases, while interfacial tensions exhibit positive deviations from the linear behavior.

The activity coefficients and boiling points of ethanol + THP were well-correlated with the liquid-phase mole fraction using the Wohl, NRTL, Wilson, and UNIQUAC equations, the best fit corresponding to the Wohl model. The excess volumes and interfacial tensions of the quoted mixture were smoothed and well-represented by the Redlich−Kister equation.

ASSOCIATED CONTENT

Supporting Information

Figures S1 to S3, which illustrate the activity coefficient plot for the system ethanol (1) + THP (2) at (50.0, 75.0, and 94.0) kPa, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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